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(54) **Detergent composition**

(57) A detergent composition comprises 0.01 to 10 percent by weight of an amphoteric copolymer obtained by co-polymerizing an anionic vinyl monomer having a

polymerizable unsaturated group with a cationic vinyl monomer having a polymerizable unsaturated group in a molar ratio of 1:99 to 99:1. The balance comprises optional additives and a carrier for the liquid or powder detergent composition.

GB 2 104 091 A

The chemical formulae appearing in the printed specification were submitted after the date of filing, the formulae originally submitted being incapable of being satisfactorily reproduced.

SPECIFICATION  
Detergent composition

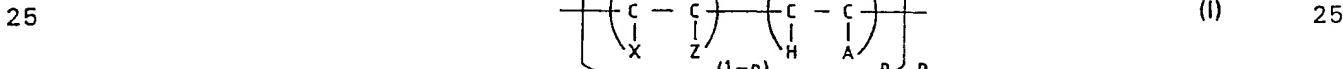
The present invention relates to a detergent composition containing a specific amphoteric polymer. More particularly, the present invention relates to a detergent composition having a deterging capacity remarkably improved by incorporating a specific amphoteric polymer obtained by copolymerizing a cationic vinyl monomer with an anionic vinyl monomer.

5 Polymers have been used as additives for detergents. For example, there have known detergent compositions containing polymers as a thickening agent stabilizer, protective colloid, builder, softener, encapsulating agent, hazing agent, pearlizing agent or skin- or hair-protecting agent. However, they have 10 been used merely according to the properties generally known as the characteristics of the high molecular compounds.

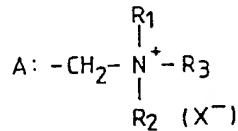
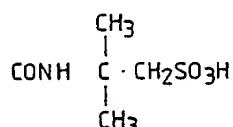
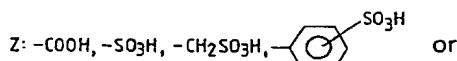
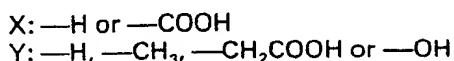
10 After investigations made for the purpose of finding a new application of polymers in detergent systems, the inventors have found that, surprisingly, a specific polymer greatly improves the detergency of a detergent composition particularly in the presence of a surfactant. The present 15 invention has been completed on the basis of this finding.

15 The present invention provides a detergent composition containing a specific amphoteric polymer obtained by copolymerizing a cationic vinyl monomer with an anionic vinyl monomer. In view of the deterging effects of the composition, it is noted that the effects of the amphoteric polymer in the present invention are utterly different from the known effects of high molecular surfactants not relating 20 directly to the detergency, such as a dispersing effect.

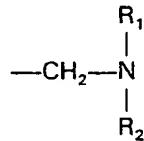
The amphoteric copolymer used in the present invention is obtained by copolymerizing an anionic vinyl monomer having a polymerizable unsaturated group with a cationic vinyl monomer having a polymerizable unsaturated group in a molar ratio of 1—99:99—1, preferably 20—80:80—20. The amphoteric copolymer thus obtained is represented by general formula (I):



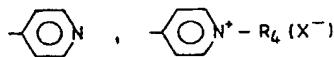
wherein:



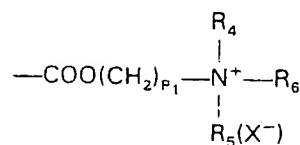
35 in which R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> each represent a C<sub>1</sub> to C<sub>3</sub> alkyl group and X<sup>−</sup> represents an anion such as a halogen or diethyl sulfate (the same shall apply hereinafter),



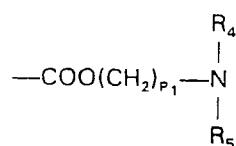
in which R<sub>1</sub> and R<sub>2</sub> each represent a C<sub>1</sub> to C<sub>3</sub> alkyl group,



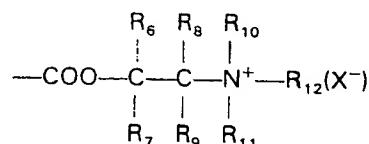
in which R<sub>4</sub> represents a C<sub>1</sub> to C<sub>3</sub> alkyl group,



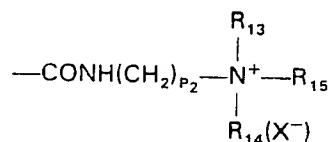
in which  $R_4$ ,  $R_5$  and  $R_6$  each represent a C<sub>1</sub> to C<sub>3</sub> alkyl group and  $P_1$  represents an integer of 2 to 4,



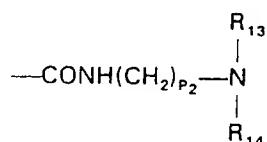
in which  $R_4$  and  $R_5$  each represent a C<sub>1</sub> to C<sub>3</sub> alkyl group and  $P_1$  represents an integer of 2 to 4,



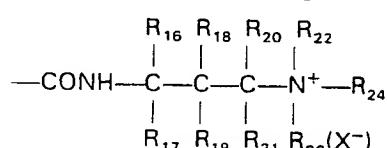
in which  $R_6$ ,  $R_7$ ,  $R_8$  and  $R_9$  each represent H or CH<sub>3</sub> and  $R_{10}$ ,  $R_{11}$ , and  $R_{12}$  each represent a C<sub>1</sub> to C<sub>3</sub> alkyl group,



in which  $R_{13}$ ,  $R_{14}$  and  $R_{15}$  each represent a C<sub>1</sub> to C<sub>3</sub> alkyl group and  $P_2$  represents an integer of 2 to 4,



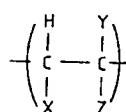
in which  $R_{13}$  and  $R_{14}$  each represent a C<sub>1</sub> to C<sub>3</sub> alkyl group and  $P_2$  represents an integer of 2 to 4, or



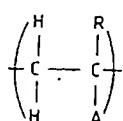
in which  $R_{16}$  to  $R_{21}$  each represents H or CH<sub>3</sub> and  $R_{22}$  to  $R_{24}$  each represents a C<sub>1</sub> to C<sub>3</sub> alkyl group  $n$  represents a number of 0.01 to 0.99,  $\rho$  represents an integer of 5 to 10000, and X, Y and Z may be an alkali metal salt, ammonium salt or alkanolamine salt.

The amphoteric polymer of the above general formula (I) according to the present invention is obtained by copolymerizing a cationic vinyl monomer with an anionic vinyl monomer. Those amphoteric polymers can be produced by a well known method. In the copolymerization, water is generally used as a solvent and potassium peroxodisulfate, potassium peroxodisulfate/sodium hydrogensulfite or hydrogen peroxide/Fe<sup>2+</sup> may be used as an initiator. The resulting copolymer may be used as such or after the purification. The purification is effected by dialysis or reprecipitation method.

The amphoteric copolymer of the present invention comprises anionic vinyl monomer structural units of the formula:



and cationic vinyl monomer structural units of the formula:



randomly arranged in a molar ratio of 1—99:99—1, preferably 20—80:80—20 to form a linear polymer having a molecular weight of 1,000 to 3,000,000. This amphoteric copolymer is produced by polymerizing a mixture of the above-mentioned anionic vinyl monomer and cationic vinyl monomer in a given ratio in the presence of a polymerization initiator in water generally under a nitrogen stream. The

5

5 polymerization is carried out generally at a temperature ranging from room temperature to 90°C for 2 to 24 h to obtain the intended copolymer having a molecular weight of preferably 3,000 to 1,000,000. Either solution polymerization or bulk polymerization method may be employed. The thus obtained copolymer may be reacted with an alkali metal hydroxide, ammonia or alkanolamine to form a salt.

5

The anionic monomer used may be any of anionic monomers having a polymerizable unsaturated group and includes acrylic acid, methacrylic acid, itaconic acid, aconitic acid, hydroxyacrylic acid, maleic anhydride, fumaric acid, vinylsulfonic acid, allylsulfonic acid, methallylsulfonic acid, styrenesulfonic acid and 2-acrylamido-2-methylpropane-sulfonic acid.

10

The cationic monomer used may be any of cationic monomers having a polymerizable unsaturated group and includes 2-vinylpyridine, 4-vinylpyridine, dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, dipropylaminoethyl methacrylate, 15 dimethylaminopropylmethacrylamide, allyldimethylamine, allyldiethylamine, allyldipropylamine, dimethallyldimethylamine, methallyldiethylamine, methallyldipropylamine and methylated, ethylated or propylated derivative thereof.

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The detergent composition of the present invention contains generally 0.01 to 10 wt.%, 20 preferably 0.05 to 5% of the amphoteric polymer.

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The detergent composition of the present invention contains 1 to 50 wt.% of a surfactant. An anionic, nonionic, cationic or amphoteric surfactant generally used in the art may be selected in the present invention suitably for the use. As the surfactant, there may be mentioned an anionic surfactant such as an alkyl sulfate, alkylbenzenesulfonate, alkylpolyoxyethylenesulfate,  $\alpha$ -olefinsulfonate, 25 alkanesulfonate, alkyl glyceryl ether sulfonate, alkyl or alkenylcarboxylate, alkenylsuccinate, N-acylsarcosinate, salt of carboxymethylated alkylpolyoxyethylene or alkylphosphate salt; a nonionic surfactant such as a fatty acid diethanolamide, dimethylalkylamine oxide, alkylpolyoxyethylene or alkylarylpolyoxyethylene; cationic surfactant such as an alkyltrimethylammonium salt, dialkyldimethylammonium salt or alkyl-(N-hydroxyethyl)-dimethylammonium salt; or an amphoteric 30 surfactant such as an alkylimidazole derivative, dimethylalkylbetaine or dimethylalkylsulfobetaine. The amphoteric polymer is used in an amount of 0.02 to 50 wt.%, preferably 0.25 to 25 wt.%, based on the surfactant according to the present invention. The amount of the surfactant may be determined suitably according to use of the detergent. In carrying out the present invention, the surfactant may be omitted in some cases.

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35 The detergent composition of the present invention may contain also other components such as a solvent, e.g. a monoalcohol, dialcohol, glycerol, ethylene glycol monobutyl ether or diethylene glycol monomethyl ether, a hydrotrope, e.g. a benzenesulfonic acid salt, p-toluenesulfonic acid salt, m-xenesulfonic acid salt or urea, a chelating agent, an antiseptic, a dyestuff, a perfume, a U.V. absorber, an antioxidant, a hazing agent or thickening agent. The detergent composition of the present invention 40 is generally in the form of a liquid prepared by adding water to the detergent composition. Further, it may be in the form of a solid.

40

The detergent composition of the present invention can be used as a detergent for metals, machines, ships, textiles, glasswares, foods, tablewares, fibers and domestic appliances as well as a shampoo base. The properties required of such a detergent include deterging power, foam-increasing 45 property and rinsing properties (defoaming property, the touch, etc.). In the present invention, the larger the amount of the amphoteric polymer, the higher the capacities such as deterging power. However, an excessive amount of the amphoteric polymer might exert a harmful influence on physical properties of the product, such as stability and viscosity.

45

The following examples of synthesis of amphoteric polymers and the examples of the present 50 invention will further illustrate the invention, which by no means limit the invention.

50

### Synthesis Example 1

600 g of ion-exchanged water, 55 g of dimethylaminoethyl methacrylate, 30 g of methacrylic acid and 0.3 g of potassium peroxodisulfate were charged in a 1 l flask provided with a stirrer, thermometer, reflux condenser and nitrogen gas inlet. The polymerization reaction was carried out at 55 70°C under a nitrogen stream for 6 h. Then, the reaction mixture was cooled to room temperature and poured into 3000 g of acetone. An amphoteric polymer thus precipitated was filtered out. The weight of the polymer after drying under reduced pressure was 83 g. The rate of polymerization was 98%.

55

### Synthesis Example 2

An anionic monomer and a cationic monomer as shown in Table 1 were copolymerized in a molar 60 ratio of 1:1 in the same manner as in the above Synthesis Example 1. The synthesis conditions were as follows:

60

5

	Ion exchanged water	600 ml
	Monomers	0.5 M
	Temperature	70°C
	Reaction time	6 h
	Initiator	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>

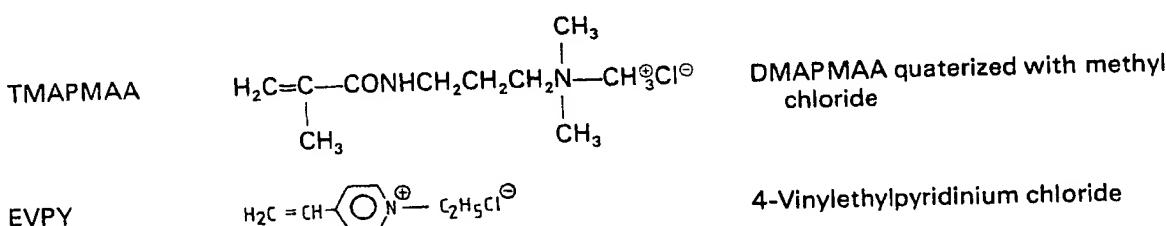
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**Table 1**  
*Synthesis No.*    *Anionic monomer*    *Cationic monomer*

10	1	AA	DMAEMA
	2	AA	TMAEMA
	3	AA	EDMAEMA
	4	MA	TMAEMA
	5	MA	EDMAEMA
	6	SS	TMAEMA
15	7	SS	TMAPMAA
	8	AAMPS	EDMAEMA
	9	AAMPS	EVPY
	10	AAMPS	TMAPMAA
	11	ALS	EDMAEMA
20	12	VS	EDMAEMA
	13	VS	DMAPMAA

wherein:

AA	$\begin{array}{c} \text{H} \\   \\ \text{H}_2\text{C}=\text{C}-\text{COOH} \end{array}$	Acrylic acid
MA	$\begin{array}{c} \text{H}_2\text{C}=\text{C}-\text{COOH} \\   \\ \text{CH}_3 \end{array}$	Methacrylic acid
SS	$\begin{array}{c} \text{H}_2\text{C}=\text{CH}-\text{C}_6\text{H}_4-\text{SO}_3\text{H} \end{array}$	Styrenesulfonic acid-(4)
AAMPS	$\begin{array}{c} \text{CH}_3 \\   \\ \text{H}_2\text{C}=\text{CH}-\text{CONH C}-\text{CH}_2\text{SO}_3\text{H} \\   \\ \text{CH}_3 \end{array}$	2-Acrylamido-2-methylpropanesulfonic acid
ALS	$\text{H}_2\text{C}=\text{CH}-\text{CH}_2\text{SO}_3\text{H}$	Allylsulfonic acid
VS	$\text{H}_2\text{C}=\text{CH}-\text{SO}_3\text{H}$	Vinylsulfonic acid
DMAEMA	$\begin{array}{c} \text{CH}_3 \\   \\ \text{H}_2\text{C}=\text{C}-\text{COOCH}_2\text{CH}_2\text{N} \begin{array}{l} \diagup \text{CH}_3 \\ \diagdown \text{CH}_3 \end{array} \end{array}$	Dimethylaminoethylmethacrylate
DMAPMAA	$\begin{array}{c} \text{CH}_3 \\   \\ \text{H}_2\text{C}=\text{C}-\text{CONHCH}_2\text{CH}_2\text{CH}_2\text{N} \begin{array}{l} \diagup \text{CH}_3 \\ \diagdown \text{CH}_3 \end{array} \end{array}$	Dimethylaminopropylmethacryamide
TMAEMA	$\begin{array}{c} \text{CH}_3 \\   \\ \text{H}_2\text{C}=\text{C}-\text{COOCH} \begin{array}{c} \text{CH}_3 \\   \\ \text{N}-\text{CH}_3^{\oplus}\text{Cl}^{\ominus} \end{array} \end{array}$	DMAEMA quaterized with methyl chloride
EDMAEMA	$\begin{array}{c} \text{CH}_3 \\   \\ \text{H}_2\text{C}=\text{C}-\text{COOCH}_2\text{CH}_2\text{N}-\text{C}_2\text{H}_5^{\oplus}\text{C}_2\text{H}_5\text{SO}_4^{\ominus} \\   \\ \text{CH}_4 \end{array}$	DMAEMA quaterized with diethyl sulfate



In the following examples wherein detergent compositions containing polymers of Synthesis Nos. 1 to 13 shown in Table 1 were tested, the properties of the detergents were examined according to the following methods:  
 5 [Test methods]

**a) Detergency**

0.1% of Sudan III (a red dyestuff) used as an indicator was added to beef tallow. 5 g of the mixture was applied to each porcelain dish (diameter: 25 cm) and rubbed with a sponge impregnated 10 with 10 g of a detergent and 20 g of water. Detergency of the detergent is represented by the number of dishes cleaned with the sponge until the beef tallow could no more be removed completely.

**b) Foaming power**

A foaming power of 0.5% detergent solution containing 0.1% of a commercially available butter as a dirt was measured. 40 cc of the butter-containing detergent solution was charged in a glass 15 cylinder having a diameter of 5 cm and the solution was stirred by means of a rotary stirrer for 10 min. Immediately thereafter, the height of the foam was measured.

**c) Water repellency**

A commercially available 200 ml glass was washed well with a cleanser. After confirming that 20 the glass could not repel water any more, the glass was rinsed with ion-exchanged water and dried. 150 ml of 1% aqueous detergent solution was charged in the glass, stirred by means of a rotary stirrer for 30 min and poured out. 200 ml of city water was charged in the glass, left to stand for 30 sec, and then poured out. This procedure was repeated three times. Water repellency after the pouring of water 20 for the fourth time and the state of the glass after left to stand for one day were observed.

**d) Rinse**

100 cc of 0.25% aqueous detergent solution (temp.: 20°C) was placed in a 500 cc separatory funnel and shaken given times. Then, the solution was poured out and the amount of the foam was measured. Thereafter, 50 cc of rinsing water (20°C) was poured thereinto and the separatory funnel was rotated slowly 10 times. This procedure was repeated until the foam disappeared to determine the 25 number of times of rinse.

**30 Example 1**

A liquid detergent of the following composition was prepared:

Sodium straight-chain alkylbenzenesulfonate	20 wt. %
Coconut fatty acid diethanolamide	5 wt. %
Polymer	1 wt. %
Water	balance

35

Detergency and foaming power of the detergent were measured to obtain the results shown in Table 2.

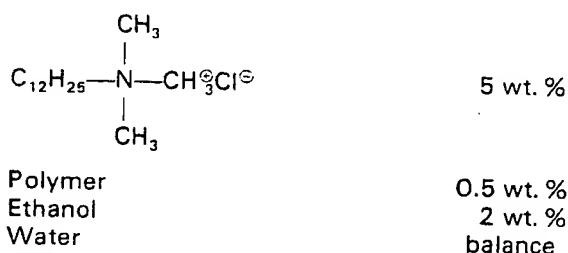
**Table 2**

40	<i>Polymer</i>	<i>Number of dishes cleaned</i>	<i>Foaming power (m/m)</i>	40
	Not used	2	55	
	Synthesis No. 1	4—5	75	
	Synthesis No. 3	7—8	80	
	Synthesis No. 4	7	95	45
	Synthesis No. 6	6	85	
45	Synthesis No. 8	5—6	80	
	Synthesis No. 10	5	85	
	Synthesis No. 12	7—8	90	

It is understood from Table 2 that the detergency and foaming power were remarkably improved 50 by the incorporation of the polymer.

### Example 2

A liquid detergent of the following composition was prepared:



Water repellency of the detergent was examined to obtain the results shown in Table 3.

Table 3

<i>Polymer</i>	<i>Water repellency</i>
Not used	observed
Synthesis No. 2	not observed
Synthesis No. 3	not observed
Synthesis No. 5	not observed

### Example 3

### 15 [Test of preference for foams]

Preference for foams were examined by a panel comprising 30 female testers. In the test, the preference for foams was examined by a pair comparison method using detergent compositions A and B in the same manner as in the deterging power test. The compositions tested are shown in Table 4 and the test results are shown in Table 5.

20 Criteria

- +2: A was preferred.
- +1: A was relatively preferred.
- 0: Preferences for A and B were equal.
- 1: B was relatively preferred.
- 2: B was preferred.

Table 4

Components	Composition No.			Comparative Example 4
	1	2	3	
Sodium alkyl ether sulfate*	20	20	20	20
Coconut fatty acid diethanolamide	5	5	5	5
Ethanol	5	5	5	5
Polymer				
Synthesis No. 3	0.3			
Synthesis No. 11		0.3		
Synthesis No. 13			0.3	
Water	balance	balance	balance	balance

**Table 5**

40	Combination (A and B)	Marks					Judgement	40
		+2	+1	0	-1	-2		
45	Compositions Nos. 1 vs. 4	9	12	7	2	0	No. 1 was preferred to No. 4 (+28)	45
	Composition Nos. 2 vs. 4	4	7	16	3	0	No. 2 was preferred to No. 4 (+12)	
	Composition Nos. 3 vs. 4	7	9	10	4	1	No. 3 was preferred to No. 4 (+17)	

(Note)\* Average carbon chain length: 12, ethylene oxide (3 mol) adduct.

### Example 4

Rinsing tests of the compositions of the present invention and polymer-free comparative compositions were carried out. The compositions are shown in Table 6 and the test results are shown in Table 7.

Table 6

Table 7

	<i>Composition No.</i>	<i>Amount of foam (ml)</i>	<i>Number of times of rinse</i>	
5	5	350	3	5
	6	350	3—4	
	7	400	3—4	
	8	350	3	
10	9	300	3	10
	10	350	4	
	11	350	4	
	12	350	3—4	
	13	400	5—6	
	14	400	6	

**Claims**

15 1. A detergent composition which comprises 0.01 to 10 percent by weight of an amphoteric copolymer obtained by co-polymerizing an anionic vinyl monomer having a polymerizable unsaturated group with a cationic vinyl monomer having a polymerizable unsaturated group in a molar ratio of 1:99 to 99:1, the balance being optional additives and a carrier for the liquid or powder detergent composition. 15

20 2. A detergent composition as claimed in Claim 1, which further comprises from 1 percent by weight to 50 percent by weight of a surfactant. 20

3. A detergent composition as claimed in Claim 2, where said amphoteric copolymer is contained in an amount of 0.02 to 50 percent by weight, based on the surfactant.

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